METHOD FOR FABRICATING A SEMICONDUCTOR STRUCTURE INCLUDING A MONOCRYSTALLINE METAL OXIDE INTERFACE WITH SILICON

Field of Invention

The present invention relates in general to a method for fabricating a semiconductor structure including a silicate interface between a silicon substrate and monocrystalline metal oxides, and more particularly to a method for fabricating an interface including a seed layer utilizing atomic layer deposition or atomic layer epitaxy.

Background of the Invention

A stable silicon (Si) surface is most desirable for subsequent epitaxial growth of metal oxide thin films on silicon for numerous device applications, e.g., ferroelectrics or high dielectric constant oxides for non-volatile high density memory and next generation MOS devices. It is pivotal to establish a stable transition layer on the Si surface for the subsequent growth of monocrystalline high-k metal oxides.

Some reported growth of these oxides, such as BaO and $BaTiO_3$ on Si (100) were based on a $BaSi_2$ (cubic) template by depositing one fourth monolayer of Ba on Si (100) using molecular beam epitaxy at temperatures greater than 850°C.

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See for example: R. McKee et al., *Appl. Phys. Lett.* 59(7), pp. 782-784 (12 August 1991); R. McKee et al., *Appl. Phys. Lett.* 63(20), pp. 2818-2820 (15 November 1993); R. McKee et al., *Mat. Res. Soc. Symp. Proc.*, Vol. 21, pp. 131-135 (1991); U.S. Patent No. 5,225,031, issued July 6, 1993, entitled "PROCESS FOR DEPOSITING AN OXIDE EPITAXIALLY ONTO A SILICON SUBSTRATE AND STRUCTURES PREPARED WITH THE PROCESS"; and U.S. Patent No. 5,482,003, issued January 9, 1996, entitled "PROCESS FOR DEPOSITING EPITAXIAL ALKALINE EARTH OXIDE ONTO A SUBSTRATE AND STRUCTURES PREPARED WITH THE PROCESS". A strontium silicide ($SrSi_2$) interface model with a c(4x2) structure was proposed. See for example: R. McKee et al., Phys. Rev. Lett. 81(14), 3014 (5 October, 1998). However, atomic level simulation of this proposed structure indicates that it likely is not stable at elevated temperatures.

Growth of $SrTiO_3$ on silicon (100) using an SrO buffer layer has been accomplished. See for example: T. Tambo et al., *Jpn. J. Appl. Phys.*, Vol. 37 (1998), pp. 4454-4459. However, the SrO buffer layer was thick (100 Å), thereby limiting application for transistor films, and crystallinity was not maintained throughout the growth.

Furthermore, $SrTiO_3$ has been grown on silicon using thick oxide layers (60-120 Å) of SrO or TiO_x. See for example: B. K. Moon et al., *Jpn. J. Appl. Phys.*, Vol. 33

(1994), pp. 1472-1477. These thick buffer layers would limit the application for transistors.

Monocrystalline high-k oxides are of great importance for the next generation MOSFET applications. In this context, the term "monocrystalline" shall have the meaning commonly used within the semiconductor industry. The term shall refer to materials that are a single crystal or that are substantially a single crystal and shall include those materials having a relatively small number of defects such as dislocations and the like as are commonly found in substrates of silicon or germanium or mixtures of silicon and germanium and epitaxial layers of such materials commonly found in the semiconductor industry. Typically, in all of these known structures, they are prepared using molecular beam epitaxy (MBE), pulsed laser deposition (PLD), sputtering, and/or metal-organic chemical vapor deposition (MOCVD). In these types of methods of preparation, it is difficult to control the silicon oxide interface to achieve low density of interfacial traps, low leakage current, and for thickness and composition uniformity over large areas, such as 8'' and above, and conformity over trenches. Accordingly, there is a need for a method that provides for a better interface between a silicon substrate and the metal oxide layer, that is conducive to the nucleation of a monocrystalline metal oxide layer, simple to manufacture, controllable, has suppressed fringing effects in MOSFET devices, and suitable for mass production.

Accordingly, it is a purpose of the present invention to provide for a method of fabricating a thin, monocrystalline stable silicate interface with silicon which would allow for the nucleation of a monocrystalline metal oxide layer on silicon.

It is yet another purpose of the present invention to provide for a method of fabricating a semiconductor structure including a monocrystalline metal oxide interface with silicon that is reliable and amenable to high throughput manufacturing.

Summary of the Invention

The above problems and others are at least partially solved and the above purposes and others are realized in a method of fabricating a semiconductor structure including the steps of providing a silicon substrate having a surface, forming on the surface of the silicon substrate, by atomic layer deposition (ALD), a seed layer comprising a silicate material and forming, by atomic layer deposition (ALD) one or more layers of a monocrystalline high dielectric constant oxide on the seed layer.

Brief Description of the Drawings

FIG. 1 illustrates a cross-sectional view of a first embodiment of a clean semiconductor substrate having a plurality of oxide layers formed thereon and in accordance with the present invention;

FIG. 2 illustrates a cross-sectional view of a semiconductor substrate having an interface seed layer formed of a silicate layer utilizing atomic layer deposition in accordance with the present invention;

FIG. 3 illustrates a cross-sectional view of second embodiment of a clean semiconductor structure having a hydrogen layer formed thereon and in accordance with the present invention;

FIG. 4 illustrates a cross-sectional view of a semiconductor structure having an oxide layer formed thereon and in accordance with the present invention;

FIG. 5 illustrates a cross-sectional view of a semiconductor substrate having an interface seed layer formed of a silicate layer utilizing atomic layer deposition in accordance with the present invention;

FIG. 6 illustrates the method of forming the interface seed layer utilizing atomic layer deposition in accordance with the present invention;

FIG. 7 illustrates a cross-sectional view of a semiconductor substrate having a high dielectric constant metal oxide layer formed on the structure illustrated in

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FIGs. 2 and 5 utilizing atomic layer deposition in accordance with the present invention;

FIG. 8 illustrates the method of forming the high dielectric constant metal oxide layer utilizing atomic layer deposition in accordance with the present invention; and

FIG. 9 illustrates a cross-sectional view of a semiconductor substrate having a monocrystalline high-k metal oxide layer formed on the structure illustrated in FIGs. 2 and 5 utilizing atomic layer deposition in accordance with the present invention.

Detailed Description of the Preferred Embodiment

A method of fabricating a high dielectric constant (high-k) metal oxide comprises an interface with a silicon substrate and is based on the use of atomic layer deposition (ALD) to form a stable silicate seed layer necessary for the subsequent growth of monocrystalline alkaline-earth metal oxide layers. Accordingly, disclosed is a new method of growing a seed layer and metal oxide layer utilizing atomic layer deposition.

To form the novel interface between a silicon (Si) substrate and one or more layers of a high dielectric constant (high-k) metal oxide, two specific approaches utilizing atomic layer deposition may be used dependent upon the substrate. A first example will be provided for starting with a Si substrate having silicon dioxide (SiO_2)

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formed on the surface. The silicon dioxide is formed as a native oxide, or by utilizing thermal, or chemical techniques. SiO_2 is amorphous rather than single crystalline and it is desirable for purposes of growing the seed layer material on the substrate to create the interfacial layer. The second example will be provided for starting with a Si substrate which undergoes hydrogen (H) passivation, thereby having formed on the surface a layer of hydrogen (H).

Turning now to the drawings in which like elements are designated with like numbers throughout the FIGs., FIG. 1 illustrates a Si substrate 10 having a surface 12, and a layer 14 of SiO_2 thereupon. In this particular embodiment, layer 14 of SiO_2 naturally exists (native oxide) once the silicon substrate 10 is exposed to air (oxygen). Alternatively, layer 14 of SiO_2 may be formed purposely in a controlled fashion well known in the art, e.g., thermally by applying oxygen onto the surface 12 at a high temperature, or chemically using a standard chemical etch process. Layer 14 is formed with a thickness in a range of 5-100Å thick, and more particularly with a thickness in a range of 10-25Å. A novel seed layer (discussed presently) is formed utilizing atomic layer deposition. First, a thin layer, less than 20Å, of a metal oxide 18, such as zirconium oxide (ZrO_2), hafnium oxide (HfO_2), strontium oxide (SrO_2), or the like, is deposited onto surface 16 of layer 14 of SiO_2 using chloride or a β-Diketonate precursor and oxygen (O_2), water

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(H_2O), nitrous oxide (N_2O), or nitric oxide (NO) at a relatively low temperature, such as less than 600°C. More particularly, Si substrate 10 and the amorphous SiO_2 layer 14 are heated to a temperature below the sublimation temperature of the SiO_2 layer 14, generally below 900°C, and in a preferred embodiment below 600°C prior to the deposition of metal oxide 18.

Next, the temperature of substrate 10 is then raised above 600°C in order for the layer 18 metal oxide (MO_x) and the layer 14 of SiO_2 to react to form a monocrystalline seed layer 20 of $MSiO_x$ (silicate), as illustrated in FIG. 2.

This step provides for the formation of a stable silicate on the silicon substrate, more particularly the formation of monocrystalline seed layer 20 having a crystal structure which will allow for the nucleation of monocrystalline metal oxide layers. The thickness of silicate, or seed, layer 20 is approximately a few monolayers, more specifically in the range of 1-50Å, with a preferred thickness in the range of 3-20Å. In this particular embodiment, the application of metal oxide 18 to the surface 16 of layer 14 and subsequent flushing with nitrogen (N_2), argon (Ar), or helium (He), and heating causes a chemical reaction, forming hafnium silicon oxide ($HfSiO_4$), zirconium silicon oxide ($ZrSiO_4$), strontium silicon oxide ($SrSiO_4$), or the like, as seed layer 20. Monitoring of the semiconductor structure can be

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accomplished utilizing any surface sensitive technique, such as reflection difference spectroscopy, spectroscopic ellipsometry, or the like wherein the surface is monitored by in situ techniques.

It should be understood by those skilled in the art that the temperatures given for these processes are recommended for the particular embodiment described, but the invention is not limited to a particular temperature or pressure range.

In an alternative embodiment, and as illustrated in FIGs. 3-6, disclosed is Si substrate 10' having a surface 12', having undergone hydrogen (H) passivation, thereby having a layer 13 of hydrogen (H) formed thereon. It should be noted that all components of FIGs. 1 and 2 that are similar to components of the FIGs. 3-5, are designated with similar numbers, having a single prime added to indicate the different embodiment. In this particular embodiment, layer 13 of hydrogen (H) is formed in a controlled fashion by hydrogen passivation techniques.

A novel seed layer (discussed presently) is formed utilizing atomic layer deposition. First, layer 13 of hydrogen (H) is desorbed from surface 12' at a high temperature, preferably in excess of 300°C. Next, surface 12' of the Si substrate 10' is exposed to a Si precursor, such as silane (SiH_4), disilane (SiH_6), or the like, and a metal precursor, such as hafnium (Hf), strontium (Sr), zirconium (Zr), or the like, generally referenced 15 of FIG. 4, during a time equal to

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T1, as shown in FIG. 6, referenced 30. Substrate 10' is exposed to the precursors at a temperature of generally between 100°C-500°, and in a preferred embodiment at a temperature of 250°C and at an atmospheric pressure of 0.5mTorr. Once the precursors are deposited, a surface 17 is flushed 32 with an inert gas, such as argon (Ar), nitrogen (N_2), or helium (He), for a time, T2, as illustrated in FIGs. 4 and 6 to remove any excess material. The stack is then exposed 34 to oxygen (O) with or without plasma, water (H_2O), nitrous oxide (N_2O), or nitric oxide (NO) for a time, T3, to oxidize layer 15 of Si and metal, thereby forming seed layer 20', generally similar to seed layer 20 of FIG. 2. Finally, seed layer 20' is flushed 36, as illustrated in FIG. 6, with argon (Ar), nitrogen (N_2) or helium (He) to eliminate any excess oxygen (O).

This step provides for the formation of a stable silicate on the silicon substrate which has been hydrogen passivated, more particularly the formation of monocrystalline seed layer 20' having a crystal structure which enables the nucleation of monocrystalline metal oxide layers. The thickness of seed layer 20' is approximately a few monolayers, more specifically in the range of 1-50 Å, with a preferred thickness in the range of 3-20Å. In this particular embodiment, the atomic layer deposition is repeated for a few cycles, preferably 4-5 cycles, to form a few monolayers. Thus, a chemical reaction takes place forming hafnium silicon oxide ($HfSiO_4$), zirconium silicon

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oxide ($ZrSiO_4$), strontium silicon oxide ($SrSiO_4$), or the like, as the seed layer 20'.

It should be understood that the component (x), where x= 0 to 1 in layer 20', having the composition of $M_xSi_{1-x}O$, can be adjusted using precursor flows of metal and silicon mixed prior to the introduction in the reaction chamber for better control. More particularly, a graded composition could be used whereby, the resultant final layer deposition using ALD renders a solely metal oxide layer, containing no silicon and having a monocrystalline surface with a known crystal structure.

Referring now to FIGs. 7, 8, and 9, the formation of monocrystalline high dielectric constant oxide layer 40 is accomplished by atomic layer deposition. First, seed layer 20 is exposed 50 to a metal precursor, such as hafnium (Hf), strontium (Sr), zirconium (Zr), lanthanum (La), aluminum (Al), yttrium (Y), titanium (Ti), barium (Ba), lanthanum scandium (LaSc), or the like, during a time, T1, thereby forming a layer 42 on surface 21 of seed layer 20. Seed layer 20 is exposed 50 to the metal precursors at a temperature of generally between 100°C-500°, and in a preferred embodiment at a temperature of 250°C and at an atmospheric pressure of 0.5mTorr. A surface 43, of layer 42 is next flushed 52 with an inert gas, such as argon (Ar), nitrogen (N2) or helium (He) for a time, T2, to remove any excess metal precursor. Finally, the semiconductor structure is exposed 54 to oxygen (O_2) with or without

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plasma, water (H2O), nitrous oxide (N_2O), or nitric oxide (NO) for a time, T3, to oxidize layer 42, more particularly the metal precursor, forming monocrystalline high-k metal oxide layer 40, as illustrated in FIG. 9. It is disclosed that high-k metal oxide layer 40 thus includes at least one of a high dielectric constant oxide selected from the group of hafnium oxide (HfO_2), zirconium oxide (ZrO_2), strontium titanate ($SrTiO_3$), lanthanum oxide (La_2O_3), yttrium oxide (Y_2O_3), titanium oxide (TiO_2), barium titanate ($BaTiO_3$), lanthanum aluminate ($LaAlO_3$), lanthanum scandium oxide ($LaScO_3$) and aluminum oxide (Al_2O_3).

As a final step, layer 40 is flushed 56 with argon (Ar), nitrogen (N_2), helium (He) or the like, to remove any excess oxygen. This atomic layer deposition is repeated for a given number of cycles to form to form a monocrystalline high-k oxide of a desired thickness.

Accordingly, disclosed is a method for fabricating a thin, seed layer 20 with silicon 10 as been described herein using atomic layer deposition (ALD). This forcing of the formation of a monocrystalline silicate layer by atomic layer deposition provides for high precision control of the thickness and composition over large areas. In addition, conformity of growth in trenches is achieved. In each cycle of the deposition process, the migration of species is enhanced on the surface.